CHAPTER 6

Time-Dependent Statistical Mechanics

6.1. More on the Langevin Equation

We now turn to the statistical mechanics of systems not in equilibrium. The first few sections are devoted to special cases, which will be used to build up experience with the questions one can reasonably ask and the kinds of answers one may expect. A general formalism will follow, with applications.

Consider first the Langevin equation, first discussed in Chapter 3, which we now write as

$$du = -au\,dt + \sqrt{2D}\,dw, \tag{6.1}$$

where w is a Brownian motion as before. A constant factor $\sqrt{2D}$ has been added in front of the noise. We want equation (6.1) to model the dynamics of a heavy particle bombarded by light particles, and the intensity of the bombardment should increase as the energy of the bombarding particles increases, that is, proportionally to D. This equation will now be fully solved.

After multiplication of equation (6.1) by e^{at} we get

$$d(ue^{at}) = \sqrt{2D}e^{at}\,dw. \tag{6.2}$$

Integrating both sides from 0 to t gives

$$\int_0^t d(ue^{as}) = \sqrt{2D}\int_0^t e^{as}\,dw.$$

Let $u(0) = b$. Then

$$u(t)e^{at} - b = \sqrt{2D}\int_0^t e^{as}\,dw.$$

After multiplying both sides by e^{-at} we obtain

$$u(t) - be^{-at} = \sqrt{2D}\int_0^t e^{a(s-t)}dw.$$

The last integral may be rewritten in the form:

$$\int_0^t e^{a(s-t)}dw = \lim_{\Delta\to 0}\sum_{j=0}^{n-1} e^{a(j\Delta-t)}(w((j+1)\Delta) - w(j\Delta)).$$

(where one does not have to worry about the Ito/Stratonovich dichotomy because the coefficient is a constant and the two formalisms are equivalent). The summands of the last sum are independent Gaussian variables with mean zero. The variance of the sum is the sum of variances of its summands, i.e.,

$$\mathrm{Var}\left(\sum_{j=0}^{n-1} e^{a(j\Delta-t)}(w((j+1)\Delta) - w(j\Delta))\right) = \sum_{j=0}^{n-1}\Delta e^{2a(j\Delta-t)}$$

and taking the limit $\Delta \to 0$ we find

$$\mathrm{Var}\left(\int_0^t e^{a(s-t)}dw\right) = \int_0^t e^{2a(s-t)}ds = \frac{1}{2a} - \frac{1}{2a}e^{-2at}.$$

As $t \to \infty$ this variance tends to $1/(2a)$. Also, as $t \to \infty$, be^{-at} tends to 0. Therefore, the solution $u(t)$ of the Langevin equation (6.1) tends to a Gaussian variable with mean 0 and variance D/a.

If the particle we are observing has mass m its energy is $\frac{1}{2}mu^2$. According to what we found in Chapter 5, the probability that the particle has velocity u is proportional to $\exp(-mu^2/2T)$. Thus, we must have

$$a = \frac{D}{Tm}.$$

The coefficient a is a friction coefficient, the relation between the friction and the temperature is an instance of a "fluctuation/dissipation theorem"; it is a consequence of the requirement that the system tend to equilibrium for long times, and relates the rate of dissipation of energy to the amplitude T of the "thermal fluctuations."

Note that we have not provided an explanation of the conditions for the validity of our modeling of the motion of a heavy particle under the influence of many others, in particular for the validity of the modeling of the interactions as white noise. This looks plausible, but should be discussed further.

The discussion of the fluctuation/dissipation theorem can be also presented in terms of the Fokker-Planck equation associated with the problem. We do that in a slightly more general case. Consider a particle

of mass m subjected to noise, with the following equations of motion

$$\dot{q} = -\frac{\partial H}{\partial p},$$
$$\dot{p} = \frac{\partial H}{\partial q} - a\frac{\partial H}{\partial q} + \sqrt{2D}\, dw(t),$$

where $H = p^2/2m + Kq^2/2$ is the Hamiltonian (making the system a harmonic oscillator), a and D are constants as in the preceding section, and $w(t)$ is BM. Substitution of the specific Hamiltonian into this equation yields

$$\dot{q} = \frac{p}{m}, \tag{6.3}$$
$$\dot{p} = -qK - a\frac{p}{m} + \sqrt{2D}\, dw. \tag{6.4}$$

Note that we still have offered no physical motivation for the use of white noise. The presence of an extra term in addition to the usual derivatives of H and to the noise is motivated by the discussion in the previous section, where a dissipation term appeared, and will be fully explained by the result below.

A slight generalization of the argument in Chapter 3 yields the following Fokker-Planck equation for the probability density $W(p, q, t)$ of p, q:

$$\frac{\partial W}{\partial t} = \frac{\partial J_1}{\partial q} + \frac{\partial J_2}{\partial p},$$

where (J_1, J_2) is the probability flux vector

$$J_1 = -p\frac{W}{m}, \quad J_2 = KqW + ap\frac{W}{m} + DWp.$$

This equation allows $W = Z^{-1}e^{-H/T}$ as a stationary density provided $a = D/T$, in agreement with the result above (in equation (6.4) the coefficient a has already been divided by m).

6.2. A Coupled System of Harmonic Oscillators

In the previous section we considered a particle acted upon by noise; the noise presumably represents an interaction with other particles, but the properties of the interaction and the validity of its description as noise were not considered. In this section we consider, in a simple case, the interaction of a singled-out particle, the "tagged" or "resolved" particle, with other particles in the framework of a Hamiltonian description of the entire system.

The particles are all in a one dimensional space; the resolved particle is located at x, has velocity v, unit mass, and is acted on by a potential

$U(x)$. It interacts with n other particles, located at q_j and having momenta p_j, with $j = 1, ..., n$. The Hamiltonian is

$$H = \frac{1}{2}v^2 + U(x) + \frac{1}{2}\sum_j p_j^2 + \frac{1}{2}\sum_j f_j^2 \left(q_j - \frac{\gamma_j}{f_j^2}x\right)^2, \tag{6.5}$$

where the f_j and γ_j are constants. The γ_j are "coupling constants", and one can check that in the absence of interaction (i.e., if one sets the coupling constants to zero) the f_j would be the frequencies of oscillation of the various particles. This Hamiltonian is quadratic (except for the term in U) so that the equations of motion for the non-resolved particles are linear; this is what makes the problem solvable explicitly. The particles with linear equations of motion of the form implied in this Hamiltonian for the unresolved particles are linear oscillators.

The equations of motion are

$$\begin{aligned}
\dot{x} &= v, \\
\dot{v} &= -\frac{dU}{dx} - \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{f_j^2}x\right), \\
\dot{q_j} &= p_j, \\
\dot{p_j} &= -f_j^2 q_j + \gamma_j x.
\end{aligned}$$

The equations of motion for the unresolved particles can be solved explicitly:

$$q_j(t) = q_j(0)\cos(f_j t) + p_j(0)\frac{\sin(f_j t)}{f_j} + \frac{\gamma_j}{f_j}\int_0^t x(s)\sin(f_j(t-s)),$$

where $q_j(0)$ and $p_j(0)$ are initial conditions (about which nothing has been said as yet). The integral term in this equation can be rewritten after integration by parts as $-\gamma_j \int_0^t v(s)\cos(f_j(t-s))/f_j^2$.

Collecting terms and inserting them into the equation for x and v one finds:

$$\dot{x}(t) = v(t), \;\; \dot{v}(t) = -U'(x) + \int_0^t K_n(t-s)v(s)ds + F_n(t), \tag{6.6}$$

where

$$K_n(t) = -\sum_j \frac{\gamma_j^2}{f_j^2}\cos(f_j t),$$

and

$$F_n(t) = \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{f_j^2}x(0)\right)\cos(f_j t) + \sum_j p_j(0)\frac{\sin(f_j t)}{f_j}.$$

Now suppose that the goal is to follow the motion of the resolved particle (the one at x with velocity v) without following the motion of all the others. Specific initial values $q_j(0)$, $p_j(0)$ cannot be take into account. The best one can do is sample these initial values for the unresolved particles from some acceptable density, which makes the whole evolution stochastic. The first term on the right-hand side of equation (6.6) is the effect of a potential which acts on the resolved particle alone at the time t, and it has no analog in the Langevin equations of the previous section. The second term on the right-hand-side of equation (6.6) is analogous to the dissipation term $-au$ in the the previous Langevin equation, and represents not only dissipation but also a memory, inasmuch as through this term the velocity at previous times impacts the current velocity. That a reduced description of the motion of the resolved variable involves a memory should be intuitively obvious: suppose you have $n > 3$ billiard balls moving about on top of a table and are trying to describe the motion of just three; the second ball may strike the seventh ball at time t_1 and the seventh ball may then strike the third ball at a later time. The third ball then "remembers" the state of the system at time t_1, and if this memory is not encoded in the explicit knowledge of where the seventh ball is at all times, then it has to be encoded in some other way. The analog of this term in the following sections will be called a "memory" term, to emphasize the possibly unfamilar memory effect. The kernel of this integral term, K_n, does not depend on the initial data and therefore this term is not random.

The last term involves the random initial data and is a random function, analogous to the white noise in the previous Langevin equation. Equation (6.6) generalizes the Langevin equation and we shall call this last term the noise term, even though in general it is not white noise. White noise can be expanded in terms of sines and cosines, but except under very special conditions the coefficients in this expansion will not be the ones in the expression for F_n above.

Finally, suppose the initial density W is $W = Z^{-1}e^{-H/T}$ with H given by equation (6.5). One can readily check that with this choice $E\left[p_j(0)p_k(0)\right] = T\delta_{jk}$, where δ_{jk} is the Kronecker δ symbol. Also,

$$E\left[\left(q_j(0) - \frac{\gamma_j}{f_j^2}x(0)\right)\left(q_k(0) - \frac{\gamma_k}{f_k^2}x(0)\right)\right] = \delta_{jk}$$

as well, where $x(0)$ is the non-random initial value of $x(t)$. With this choice of initial W one can also check that:

$$E[f_n(t)f_n(t-t')] = TK_n(t-t').$$

This is the fluctuation/dissipation theorem relevant to the present problem. It emerges simply as a consequence of the equations of motion combined with the canonical choice of initial density.

It should be noted that the problem in this section is not an equilibrium problem because the Hamiltonian depends on the variable x and changes in time. As time advances the values of the variable x become increasingly uncertain and the system "decays" to equilibrium; this decay is represented by the memory and noise.

6.3. Mathematical Addenda

A pattern has emerged in the questions asked so far in the present chapter: we consider problems with many variables where thermal equilibrium has not been established, i.e., where there is no probability density invariant in time. Such a density may be established in the future of the systems under study, this fact has present consequences, but there is no universal recipe for the evolution of the probability density and no analog of an ergodic hypothesis to simplify calculations. What one strives for is a reduced, practical description of key variables—the analog of what was called renormalization in the equilibrium case. The reduced equations we have derived replace those parts of the system that are not fully described by a pair of matched terms, a stochastic term that can be called "noise" and a damping, or "memory" term; they have to be matched to preserve the possibility of future equilibrium; the matching conditions are called "fluctuation/dissipation theorems." We now propose to derive these results in some generality; however, before we can embark on this analysis, some mathematical addenda are needed.

6.3.1. How to write a nonlinear system of ordinary differential equations as a linear partial differential equation. Consider a system of ordinary differential equations

$$\frac{d}{dt}\phi(x,t) = R(\phi(x,t)), \quad \phi(x,0) = x, \tag{6.7}$$

where R, ϕ, and x are (possibly infinite dimensional) vectors with components R_i, ϕ_i, and x_i.

We claim that this nonlinear system can be rewritten as a linear partial differential equation. This is not an approximation, but an exact representation; the cost of getting a linear system is the greater conceptual and practical complexity of having to deal with a partial differential equation.

Define the Liouville operator (as in Chapter 5):

$$L = \sum_i R_i(x) \frac{\partial}{\partial x_i}.$$

It is not assumed here that the system (6.7) is Hamiltonian, so that the coefficient functions in L are not derivatives of some H as in Chapter 5. The variables in the coefficients and in the differentiations belong to a space with as many dimensions as the space of initial data for (6.7). Now form the differential equation

$$u_t = Lu, \tag{6.8}$$

with initial data $u(x,0) = g(x)$. This is also called a Liouville equation, though the sign of the right hand side is the opposite of the one in front of the right hand side of the Liouville equation for the probability density in Chapter 5. The claim is that the solution of this equation is $u(x,t) = g(\phi(x,t))$, where $\phi(x,t)$ is the solution of the system (6.7) with initial data x. If this is true, one can clearly solve the partial differential equation (6.8) if one can solve the system of ordinary differential equations; the ordinary differential equations (6.7) are the characteristic equations of the partial differential equation (6.8).

First we prove the following useful identity:

$$R(\phi(x,t)) = D_x\phi(x,t)R(x). \tag{6.9}$$

In this formula $D_x\phi(x,t)$ is the Jacobian of $\phi(x,t)$

$$D_{x_j}\phi_i(x,t) = \frac{\partial \phi_i}{\partial x_j}$$

and the multiplication on the right hand side is a matrix vector multiplication; the left hand side is the vector R evaluated when the argument is ϕ, while on the right the argument of R is x, the initial datum of ϕ; ϕ is assumed to satisfy equations (6.7).

Define $F(x,t)$ to be the difference of the left hand side and the right hand side of (6.9)

$$F(x,t) = R(\phi(x,t)) - D_x\phi(x,t)R(x).$$

Then at $t = 0$ we have

$$\begin{aligned} F(x,0) &= R(\phi(x,0)) - D_x\phi(x,0)R(x) \\ &= R(x) - D_x(x)R(x) \\ &= R(x) - IR(x) \\ &= 0. \end{aligned} \tag{6.10}$$

Differentiating F with respect to t we get

$$\begin{aligned}
\frac{\partial}{\partial t}F(x,t) &= \frac{\partial}{\partial t}R(\phi(x,t)) - \frac{\partial}{\partial t}(D_x\phi(x,t)R(x)) \\
&= \frac{\partial}{\partial t}R(\phi(x,t)) - \frac{\partial}{\partial t}\left(D_x\phi(x,t)\right)R(x) \\
&= (D_xR)(\phi(x,t))\frac{\partial}{\partial t}\phi(x,t) - D_x\left(\frac{\partial}{\partial t}\phi(x,t)\right)R(x) \\
&= (D_xR)(\phi(x,t))\frac{\partial}{\partial t}\phi(x,t) - D_x(R(\phi(x,t)))R(x) \\
&= (D_xR)(\phi(x,t))R(\phi(x,t)) - (D_xR)(\phi(x,t))D_x\phi(x,t)R(x) \\
&= (D_xR)(\phi(x,t))\left(R(\phi(x,t)) - D_x\phi(x,t)R(x)\right) \\
&= (D_xR)(\phi(x,t))F(x,t). \qquad (6.11)
\end{aligned}$$

From (6.10) and (6.11) one can conclude that $F(x,t) \equiv 0$. Indeed, the initial value problem defined by (6.10) and (6.11) has a unique solution given that R and ϕ are smooth. Since $F(x,t) = 0$ solves this problem we have proved (6.9).

Take an arbitrary smooth function $g(x)$ on Γ and form the function

$$u(x,t) = g(\phi(x,t)).$$

Clearly $u(x,0) = g(x)$. Differentiate this function with respect to t using the chain rule

$$\frac{\partial u}{\partial t} = \sum_i \frac{\partial g(\phi(x,t))}{\partial x_i}\frac{\partial \phi_i(x,t)}{\partial t} = \sum_i R_i(\phi(x,t))\frac{\partial g(\phi(x,t))}{\partial x_i}.$$

Using the formula (6.9) this last expression becomes

$$\begin{aligned}
&\sum_i \left(\sum_j \frac{\partial \phi_i(x,t)}{\partial x_j}R_j(x)\right)\frac{\partial g(\phi(x,t))}{\partial x_i} \\
&= \sum_j R_j(x)\left(\sum_i \frac{\partial g(\phi(x,t))}{\partial x_i}\right)\frac{\partial \phi_i(x,t)}{\partial x_j} = \sum_j R_j(x)\frac{\partial g(x,t)}{\partial x_j} = Lu. \qquad (6.12)
\end{aligned}$$

Hence $u(x,t) = g(\phi(x,t))$ is the (unique) solution of the equation

$$u_t = Lu, \quad u(x,0) = g(x). \qquad (6.13)$$

Clearly, if one can solve the system (6.7) for all x one can solve the Liouville equation (6.13) for any initial datum g. Conversely, suppose one can solve the Liouville equation for all initial data g; pick $g(x) = x_j$; the solution of the Liouville equation is then $\phi_j(x,t)$, the j-th component of the solution of the system of ordinary differential equations (6.7).

If L is skew-symmetric, the equation for the probability density in Chapter 5 and the Liouville equation here which is equivalent to the original system differ by a sign. By judicious insertions of factors of complex i one can get the two Liouville equations to be adjoint; the two equations are then related like the Schroedinger and Heisenberg representations in quantum mechanics.

6.3.2. More on the semigroup notation. In Chapter 3 we introduced the semigroup notation, according to which the solution of (6.13) is denoted by $e^{tL}g$; the time dependence is explicitly marked, and the value of this solution at a point x is denoted by $e^{tL}x$. with this notation the formula for the solution $u(x,t) = u(\phi(x,t))$ of (6.13) becomes:

$$e^{tL}g(x) = g(e^{tL}x). \tag{6.14}$$

Note that $e^{tL}x$ is not e^{tL} evaluated at x but e^{tL} acting on the vector whose components are the functions x_i; the time propagation of a function g commutes with the time propagation of the initial conditions x_i. Equation (6.12) becomes simply

$$Le^{tL} = e^{tL}L. \tag{6.15}$$

The analogous formula for matrices is of course obvious.

Consider the differential equation $u_t = Au + Bu$, where A and B are operators and u is a function of x and t. The solution of $u_t = Au$, $u(0) = u_0$ is $u(t) = e^{tA}u_0$; to solve $u_t = Au + Bu$ use the method of variation of constants: Let $u = we^{tL}u_0$, and substitute into the equation; a short manipulation yields:

$$u(t) = e^{tL}u_0 + \int_0^t u(t-s)Be^{sA}u_0\,ds,$$

(where the argument x is not explicitly written) or

$$e^{t(A+B)} = e^{tA} + \int_0^t e^{(t-s)(A+B)}Be^{sA}ds.$$

This formula is often called the "Duhamel formula" or, in physics, the "Dyson formula." If the operators are finite dimensional the formula can be checked by even more elementary means.

6.3.3. Hermite polynomials and projections. The polynomials orthonormal with respect to the inner product

$$(u,v) = \int_{-\infty}^{+\infty} \frac{e^{-x^2/2}}{\sqrt{2\pi}}u(x)v(x)dx$$

are called the Hermite polynomials. One can generalize them to spaces with more dimensions: If one defines the inner product

$$(u,v) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} (2\pi)^{-n/2}\, e^{-(\sum x_i^2)/2} u(x)v(x)dx_1 \cdots dx_n,$$

then one finds that the following polynomials form an orthonormal family: First the constant polynomial 1; then the n linear monomials $x_1, x_2, \ldots, x_n$; then the polynomials of degree 2: $H_2(x_1) = x_i x_j$ for $i \neq j$, etc. More generally, if $H(q,p)$ is a Hamiltonian, one can define a family of polynomials in the variables q, p that are orthonormal with respect to the canonical density $Z^{-1}e^{-H/T}$. We shall still call these polynomials "Hermite polynomials", and we shall do the same for polynomials orthonormal with respect to an inner product with a weight W.

Consider an n-dimensional space Γ with a probability density W. Divide the coordinates into two groups, $\hat{x}$ and $\tilde{x}$. Let g be a function of x; then $\mathbb{P}g = E[g|\hat{x}]$ is an orthogonal projection onto the subspace of functions of $\hat{x}$. One can perform this projection by spanning that subspace by those Hermite polynomials that are functions of $\hat{x}$ and using them as in Chapter 1. One can then approximate the "conditional expectation" projection by a "finite-rank" projection in which one uses only a fixed set of Hermite polynomials. A particular finite rank projection widely used in physics is the one in which only the Hermite polynomials of degree one are used; this is also known as the "linear" projection (as if other projections were not linear). We have already used a linear projection implicitly in the "linear" prediction method in Chapter 4.

6.4. The Mori-Zwanzig formalism

Return now to the system

$$\frac{d\phi_i(x,t)}{dt} = R(\phi(x,t)), \quad \phi_i(x,0) = x_i, \quad 1 \leq i \leq n. \tag{6.16}$$

Suppose one is interested only in the first m variables $\phi_1, \ldots, \phi_m$, with $m < n$; partition the vector ϕ as in Chapter 5 into "resolved" variables $\hat{\phi}$ and "unresolved" variables $\tilde{\phi}$ so that

$$\phi = (\hat{\phi}, \tilde{\phi}), \quad \hat{\phi} = (\phi_1, \ldots, \phi_m), \quad \tilde{\phi} = (\phi_{m+1}, \ldots, \phi_n),$$

and similarly $x = (\hat{x}, \tilde{x})$ and $R = (\hat{R}, \tilde{R})$. We now look for equations for the components $\hat{\phi}(t)$ with the initial conditions $\hat{\phi}(0) = \hat{x}$. We further assume that at time $t = 0$ we know the joint pdf of all the variables x; once the initial data $\hat{x}$ are given, the pdf of the variables in $\tilde{x}$ is

the joint pdf of all the x variables conditioned by $\hat{x}$. Something has to be assumed about the missing variables $\tilde{x}$ less the problem become meaningless; the assumptions here are often realistic, but one should be careful not to use what is now coming when these assumptions do not hold.

Form the Liouville equation $u_t = Lu$ as above; the components $\hat{\phi}$ are $\hat{\phi}_j(x,t) = e^{tL}x_j$ (note that $\hat{\phi}_j$ depends on all the data x when the system is not linear; if $\tilde{x}$ is random, $\hat{\phi}$ is random as well). By definition,

$$\frac{\partial}{\partial t}e^{tL}x_j = Le^{tL}x_j = e^{tL}Lx_j, \tag{6.17}$$

where the last equality is the commutation rule (6.15). Let $\mathbb{P}$ be the conditional expectation projection $\mathbb{P}g(x) = E[g|\hat{x}]$, where the probability density is the assumed density for the initial conditions. We shall use the same notation even when we later approximate the conditional expectation by a finite-rank projection. The "conditioning variables" (in terms of which $\mathbb{P}g$ will be expressed) here are the initial data, rather than the current values of $\hat{\phi}$ as in the renormalization analysis in Chapter 5; this must be so because we are assuming that some of the initial values are known and therefore the initial density is not invariant even when the system is Hamiltonian (and we are not assuming that the system (6.7) is Hamiltonian). Without an invariant measure there is no good way to determine the $\mathbb{P}$ of Chapter 5 thus our $\mathbb{P}$ here is not the same as that in Chapter 5. Note also that the $\mathbb{P}$ here is a projection on a space of functions of a fixed set of variables and is therefore time-independent. Furthermore, objects such as $\mathbb{P}\hat{\phi}(t) = E[\hat{\phi}(t)|\hat{x}]$ are of great interest: they are the best estimates of the future values of a reduced system of variables given partial information about the present. This is the kind of thing a meteorologist, for example, wants to calculate: a best prediction of a set of interesting features of the future weather given our limited information about the present state of the atmosphere.

Define furthermore $\mathbb{Q} = I - \mathbb{P}$ and keep in mind that $\mathbb{P}^2 = \mathbb{P}$, $\mathbb{Q}^2 = \mathbb{Q}$, and $\mathbb{P}\mathbb{Q} = 0$ as must be true for any projection. Equation (6.17) can be rewritten as

$$\frac{\partial}{\partial t}e^{tL}x_j = e^{tL}\mathbb{P}Lx_j + e^{tL}\mathbb{Q}Lx_j. \tag{6.18}$$

Consider the first term. We have

$$Lx_j = \sum_i R_i(\partial/\partial x_i)x_j = R_j(x);$$

and so $\mathbb{P}Lx_j = E[R_j x|\hat{x}] = \bar{R}_j(\hat{x})$ is a function of the reduced set of variables $\hat{x}$, the average of the initial data conditioned by the partial knowledge embodied in $\hat{x}$; $e^{tL}\mathbb{P}Lx_j = \bar{R}_j(\hat{\phi}(x,t))$ by the commutation rule (6.14). If one replaces the projection used here by the projection of Chapter 5 one finds that equation (6.18) coincides with the equation we used to renormalize in Chapter 5 provided $\mathbb{Q} = 0$; but $\mathbb{Q} \neq 0$ unless $\hat{\phi}$ coincides with ϕ which explains why the "equilibrium" renormalization of Chapter 5 has to be reformulated here before one can deal with time dependent statistics.

We now split the second term in equation (6.18) using Dyson's formula with $A = \mathbb{Q}L$ and $B = \mathbb{P}L$ (the reasons for the split will emerge soon)

$$e^{tL} = e^{t\mathbb{Q}L} + \int_0^t e^{(t-s)L}\mathbb{P}Le^{s\mathbb{Q}L}ds. \tag{6.19}$$

Here the linearity of the Liouville equation is being used–this step is the motivation for the introuction of that equation into the analysis. Using (6.19), equation (6.18) becomes

$$\frac{\partial}{\partial t}e^{tL}x_j = e^{tL}\mathbb{P}Lx_j + e^{t\mathbb{Q}L}\mathbb{Q}Lx_j + \int_0^t e^{(t-s)L}\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j ds. \tag{6.20}$$

This is the Mori-Zwanzig equation. This equation is exact and is an alternative way of writing the original system (6.16). It is an equation for each one of the $\phi_j(x,t) = e^{tL}x_j$, $j = 1,\dots,m$.

Now examine the different terms that appear in the right hand side of (6.20). The first term is a function only of $\hat{\phi}(x,t)$ and represents the self-interaction of the resolved variables; it is a Markovian term, inasmuch as it is evaluated at the same time t as the left hand side of the equation.

To decode the second term, write

$$e^{t\mathbb{Q}L}\mathbb{Q}Lx_j = w_j.$$

The function $w_j(x,t)$ satisfies by definition the equation

$$\begin{aligned} &\frac{\partial}{\partial t}w_j(x,t) = \mathbb{Q}Lw_j(x,t) \\ &w_j(x,0) = \mathbb{Q}Lx_j = (I-\mathbb{P})R_j(x) = R_j(x) - \bar{R}_j(\hat{x}). \end{aligned} \tag{6.21}$$

If one identifies $\mathbb{P}Lx_j$ as the "average of the initial data" then $w_j(x,0)$ is a "fluctuating part of the initial data" (according the often used terminology in which a "fluctuating part" of a random variable η is $\eta - E[\eta]$). Obviously, $\mathbb{P}w_j(x,0) = 0$. If one took this initial function and applied the operator e^{tL} to it (i.e., solved the Liouville equation starting from this initial function), the result would in general have a

non-trivial mean part (one not in the null-space of $\mathbb{P}$); the evolution equation for w_j removes the "mean part" at each instant of time. As a result, $\mathbb{P}w_j(x,t) = 0$ for all time t.

Call the space of functions of $\hat{x}$ the "resolved subspace" and its orthogonal complement (with respect to the inner product defined by the initial density) the "noise subspace." $\mathbb{P}$ applied to any element of the noise subspace gives zero, and similarly $\mathbb{Q}$ applied to any element of the resolved subspace gives zero. The functions $w_j(x,t) = e^{t\mathbb{Q}}\mathbb{Q}Lx_j$ are in the noise space; we shall call the vector of which they are the components the "noise" for short. The noise is determined by the initial data and by the system (6.16) and does not have to be white noise. Equation (6.21) is the "orthogonal dynamics" equation.

The third term in equation (6.20) is the "memory" term because it involves integration of quantities which depend on the state of the system at earlier times. To see what this term does, approximate the projection $\mathbb{P}$ by a finite rank projection in terms of Hermite polynomials $(H_1, \ldots, H_p)$ (whose arguments belong to $\hat{x}$). We have

$$\begin{aligned}\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j &= \mathbb{P}L(\mathbb{P}+\mathbb{Q})e^{s\mathbb{Q}L}\mathbb{Q}Lx_j \\ &= \mathbb{P}L\mathbb{Q}e^{s\mathbb{Q}L}\mathbb{Q}Lx_j \\ &= \sum_{k=1}^{p}(L\mathbb{Q}e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, H_k(\hat{x}))H_k(\hat{x}).\end{aligned}$$

To simplify the analysis, assume that L is skew symmetric, $(u, Lv) = -(Lu, v)$; we have seen that this includes the case where the system (6.16) we started from was Hamiltonian. Then we find:

$$\begin{aligned}(L\mathbb{Q}e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, H_k(\hat{x}) &= -(\mathbb{Q}e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, LH_k) \\ &= -(e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, \mathbb{Q}LH_k).\end{aligned}$$

Both $\mathbb{Q}Lx_j$ and $\mathbb{Q}LH_k$ are in the noise subspace, and $e^{s\mathbb{Q}L}\mathbb{Q}Lx_j$ is a solution at time s of the orthogonal dynamics equation with data in the noise subspace; $\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j$ is then a sum of temporal covariance of "noises," i.e., of functions in the noise subspace. The operator $e^{(t-s)L}$ commutes with each $(L\mathbb{Q}e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, H_k(\hat{x}))$ because the latter expression is an inner product which does not evolve in time, and by the rule (6.14) one finds $e^{(t-s)}H_k\hat{x} = H_k\hat{\phi}(t-s)$; if one makes the change of variables $t' = t - s$ and drops the prime, one finds that the memory integral is a sum of time covariances of noises with time difference s multiplying variables that describe the state of the system at time s. The split (6.19) was introduced so as to divide the non-Markovian term

in the equation of motion for the $\hat{\phi}$ into a noise and a memory that depends on the temporal covariances of noise.

One can bring in an apparent simplification by multiplying equation (6.20) by the projection $\mathbb{P}$; remember that $\mathbb{P}$ is time invariant, so that $\mathbb{P}(\partial/\partial t)\hat{\phi}$ becomes $(\partial/\partial t)E[\hat{\phi}|\hat{x}]$—a quantity of some interest. Using the fact that $\mathbb{P}$ operating on the noise term is zero yields

$$\frac{\partial}{\partial t}\mathbb{P}e^{tL}x_j = \mathbb{P}e^{tL}\mathbb{P}Lx_j + \int_0^t \mathbb{P}e^{(t-s)L}\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j ds. \tag{6.22}$$

where $\mathbb{P}e^{tL}x_j = E[\hat{\phi}(x,t)|\hat{x}]$ by definition. However, the Markovian term is now more complicated: we have seen that $e^{tL}\mathbb{P}Lx_j$ is in general a nonlinear function $\bar{R}(\hat{\phi}(t))$; however, $\mathbb{P}\bar{R}(\hat{\phi}(t))$ is in general not equal to $\bar{R}(\mathbb{P}\hat{\phi}(t))$ and some approximation scheme must be devised.

To make contact with earlier work, one has to make some drastic simplifications. Assume that the "linear" projection will do the job (this is generally true if the processes ϕ have small amplitude). Suppose that the initial probability density W is such that $E[x_i x_j] = (x_i, x_j) = \delta_{ij}$. Assume that the noise $e^{t\mathbb{Q}L}\mathbb{Q}Lx_j$ is white noise (occasionally this is a good assumption, see the next few sections). Then the correlations which appear in the integrand of the memory term are delta functions and in this case the memory term has no memory. With some further assumptions about the original equations (6.16) one recovers as special cases the systems of the first two sections of this chapter. Thus equations (6.20) are general Langevin equations, generalizing what we have earlier called the Langevin equation. Fluctuation/dissipation relations follow automatically.

These expressions are exact. If one has a system of equations for ϕ, a pdf for the initial data, specific initial data for $\hat{\phi}(t=0)$, and one wants to find $\hat{\phi}(t)$, one can either sample the whole vector of initial data, solve for $\phi(t)$, and throw away all that is not $\hat{\phi}$, or one can solve equations (6.20). One can average in either case. Equations (6.20) are fewer in number but this advantage is outweighed by the need to know the noise and the covariance functions. What equations (6.20) do provide is a starting point for approximation.

What are such approximations needed for ? There are two settings in which they can be useful:

(1) The analysis of how large mechanical systems converge to the kind of equilibrium discussed in the previous Chapter. If one sets the values of some initial data to fixed values but lets the other initial values be picked at random from a canonical density, one in fact takes the mechanical system out of equilibrium

at time $t = 0$. An ergodic Hamiltonian system will then see its entropy increase and it will tend towards equilibrium; it is often of interest to see how this happens and this can in principle be done by approximating equation (6.20) that correspond to the dynamics of the system.

(2) Suppose one wants to make predictions on the basis of partial data (as for example in weather forecasting). One can assume something reasonable about the missing information, for example on the basis of previous experience, and turn to equations (6.20). Prediction methods based on the Mori-Zwanzig formalism also go under the name "optimal prediction."

Finally, some words on the long-time behavior of the solutions of (6.20). Suppose the system (6.16) is Hamiltonian and ergodic. If the initial data are non-equilibrium data (not sampled from a canonical density, for example some of them are given numbers $\hat{x}$), then as time unfolds the system will approach equilibirum (i.e., the joint density of the $\phi(t)$ will approach a canonical density as the entropy increases). The averages $\mathbb{P}\phi(t) = E[\phi|\hat{x}]$ will converge to the averages of ϕ with respect to the canonical density—the predictive power of initial data decays to zero with time (for example, one can make decent one-day weather forecasts on the basis of today's observations, but very poor one-year forecasts). The solutions of the equation for $\mathbb{P}\hat{\phi}(t)$ tend to constants (usually zero) independent of the data. The Markovian term in equation (6.20) tends to zero as well, and one is left with an equation that merely balances noise and memory.

6.5. Scale Separation and Weak Coupling

There are situations where one knows that the noise term in the Mori-Zwanzig equations can be approximated by white noise, and then the memory term becomes local in time and everything is simpler. This happens in particular when there is scale separation between the resolved and unresolved variables. This means that there is a significant gap between the frequencies of the resolved components $\hat{\phi}$ and the frequencies of the unresolved components $\tilde{\phi}$. The heuristic reason is clear: if the resolved variables take a time Δt to vary significantly, during this time interval the unresolved variables make many uncorrelated contributions to the motion of the resolved variables, whose effect can be described by a sum of independent Gaussian variables (by the central limit theorem) and hence summarized as the effect of a white noise. A closely related situation is that of "weak coupling", where the variations of $\tilde{\phi}$ affect $\hat{\phi}$ by a small amount; it takes many of them to have a

significant effect and their cumulative effect is that of a large number of independent contributions. The detailed description of these situations requires asymptotic solutions of a singular pertubation problems, as we illustrate by an example.

Consider a particle at a point x whose velocity v can be either $+1$ or -1; it jumps from one value to the other in every short time interval dt with a probability dt, with independent probabilities for a jump on two disjoint intervals. Let the position x of the particle be given by

$$\dot{x} = \epsilon v(t),$$

or

$$x(t) = \epsilon \int_0^t v(s)ds.$$

The presence of the parameter ϵ, which will soon be made small, embodies a weak coupling assumption. The variable x is analogous to a resolved variable; for simplicity we present a model in which the unresolved, "fast", variable v is not determined by an equation but rather by fiat.

The probability density function $W(x, \pm 1, t)$ is the probability that the particle be between x and $x + dx$ while v is either $+1$ or -1. It can be thought of as a vector $W = (W^+, W^-)$, where $W^+(x, t)$ is the probability that the particle be between x and $x+dx$ with $v = +1$ with a similar definition for W^-. $W^+(x, t+\delta t)$ equals $(1-\delta t)$ (the probability that there is no change in velocity) times $W(x - \delta t)$ (because particles moving at speed 1 go from $x - \delta t$ to x in a time δt), minus $\delta t W^+(x, t)$ (the probability of loss of particles to the W^- branch times the density), plus $\delta t W^-(x, t)$ (because of jumps from the minus state). Collecting terms, expanding $W(x - \delta t)$, dividing by δt and letting $\delta t \to 0$, as in Chapter 3, yields,

$$W^+_t = -W^+_x + W^- - W^+,$$

and similarly,

$$W^-_t = W^-_x + W^+ - W^-,$$

where the subscripts x, t denote differentiation. Define

$$U = W^+ - W^-, \;\; V = W^+ + W^-$$

one finds

$$U_t = \epsilon U_x - 2V_t, \;\; V_t = -U,$$

and hence,

$$U_{tt} = \epsilon U_{xx} - 2U_t.$$

Once U is found V, W^+, and W^- follow immediately.

One does not expect, with the weak coupling when ϵ is small, to have a significant displacement x of a particle when t is of order 1. We therefore introduce a slow time scale such that, when a unit time has passed on this slower scale, one can expect a significant displacement to have occurred; we do this by setting $\tau = \epsilon^2 t$; the equation for $U = U(x, \tau)$ becomes

$$\epsilon U_{\tau\tau} = U_{xx} - 2U_\tau,$$

and, in the limit $\epsilon \to 0$, we obtain $U_\tau = \frac{1}{2} U_{xx}$, a heat equation which can be solved by examining particles undergoing BMs, as promised. This is of course just a reflection of the fact that by the central limit theorem the sum of the independent contributions to x due to the assumed velocity adds up over time to a Gaussian variable.

Similarly, one can see that a heavy particle bombarded by lighter particles undergoes a displacement which, over the proper time scales, satisfies the Langevin equation as written in the first section of this chapter. The ratio of masses provides the needed ϵ.

6.6. Non-Instantaneous Memory

In the previous section we considered situations where the memory could be viewed as having zero range, i.e., where the covariances which appear in the Mori-Zwanzig identity can be viewed as δ functions. We now consider problems where the memory, while still short, has non-zero support (i.e., it has a non-negligible amplitude within an interval of time of non-zero length).

The approximation we shall examine is some detail is

$$e^{t\mathbb{Q}L} \cong e^{tL}, \tag{6.23}$$

and we consider under what conditions this is a reasonable ansatz. We pick this particular ansatz for analysis because the resulting analysis is reasonably illuminating. First note that this is a weak coupling anzatz. It is an identity in those cases where the resolved and unresolved variables do not interact, in which case the noise subspace and the resolved subspace evolve separately and there is not need to reproject the noise by $\mathbb{Q}$ to generate $e^{t\mathbb{Q}L}$.

The memory term in the Mori-Zwanzig equations (6.20) can be rewritten as

$$\int_0^t e^{(t-s)L} \mathbb{P} L e^{s\mathbb{Q}L} \mathbb{Q} L x_j \, ds = \int_0^t e^{(t-s)L} \mathbb{P} L \mathbb{Q} e^{s\mathbb{Q}L} \mathbb{Q} L x_j \, ds,$$

where the insertion of the extra $\mathbb{Q}$ is legitimate since $e^{s\mathbb{Q}L}$ maps functions in the null space of $\mathbb{P}$ back into the same subspace. Adding and

subtracting equal quantities, we find

$$\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j = \mathbb{P}L\mathbb{Q}e^{sL}\mathbb{Q}Lx_j + \mathbb{P}L\mathbb{Q}(e^{s\mathbb{Q}L} - e^{sL})\mathbb{Q}Lx_j.$$

A Taylor series yields

$$e^{s\mathbb{Q}L} - e^{sL} = I + s\mathbb{Q}L + \cdots - I - sL - \cdots = -s\mathbb{P}L + O(s^2),$$

and therefore, using $\mathbb{Q}\mathbb{P} = 0$, we find:

$$\int_0^t e^{(t-s)L}\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j\, ds = \int_0^t e^{(t-s)L}\mathbb{P}L\mathbb{Q}e^{sL}\mathbb{Q}Lx_j\, ds + O(t^3).$$

If $\mathbb{P}$ is a finite rank projection then

$$\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j = \sum_k (\mathbb{Q}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j, H_k)H_k(\hat{x})$$

where, as before, one can write

$$(\mathbb{Q}Le^{s\mathbb{Q}L}\mathbb{Q}Lx_j, H_k) = -(e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, \mathbb{Q}LH_k)$$

when L is skew-symmetric. If the correlations $(e^{s\mathbb{Q}L}\mathbb{Q}Lx_j, \mathbb{Q}LH_k)$ and $(e^{sL}\mathbb{Q}Lx_j, \mathbb{Q}LH_k)$ are significant only over short times s, the approximation (6.23) provides an acceptable approximation without requiring the solution of the orthogonal dynamics equation. This is still a short-correlation time approximation but no longer a δ-function approximation for the correlations.

One way of using the ansatz (6.23) is as follows: rewrite the memory term as

$$\int_0^t e^{(t-s)L}\mathbb{P}Le^{s\mathbb{Q}L}\mathbb{Q}R_j(x)ds = \int_0^t Le^{(t-s)L}e^{s\mathbb{Q}L}\mathbb{Q}R_j(x)ds - \int_0^t e^{(t-s)L}e^{s\mathbb{Q}L}\mathbb{Q}L\mathbb{Q}R_j(x)ds,$$

where we have used the commutation of L and $\mathbb{Q}L$ with e^{tL} and $e^{t\mathbb{Q}L}$ respectively. At this point, make the approximation (6.23) and replace the evolution operator of the orthogonal dynamics by the evolution operator of the Liouville equation. The dependence on s in the integrands disappears and all one is left with is the factor t multiplying a function of the instantaneous values of $\hat{\phi}$ equal to $e^{tL}L\mathbb{Q}Lx_j$. All that remains of the integration in time is the coefficient t. One can get rid of the noise term by premultiplying the equations by a projection $\mathbb{P}$, as in equation (6.22), and obtain a reduced non-autonomous set of differential equations.

As an example, consider the Hald model, which is a system of two linear oscillators with a nonlinear coupling, whose Hamiltonian is

$$H(\phi) = \frac{1}{2}\left(\phi_1^2 + \phi_2^2 + \phi_3^2 + \phi_4^2 + \phi_1^2\phi_3^2\right),$$

with (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4) canonical pairs of coordinates. The resulting equations of motion are:

$$\frac{d}{dt}\phi_1 = \phi_2, \quad \frac{d}{dt}\phi_2 = -\phi_1(1+\phi_3^2)$$
$$\frac{d}{dt}\phi_3 = \phi_4, \quad \frac{d}{dt}\phi_4 = -\phi_3(1+\phi_1^2).$$

Suppose one wants to solve only for $\hat{\phi} = (\phi_1, \phi_2)$, with initial data $\hat{x} = (x_1, x_2)$. Assume the initial data (x_3, x_4) are sampled from a canonical density with temperature $T = 1$. A quick calculation yields

$$E[x_3^2 | x_1, x_2] = \frac{1}{1+x_1^2}.$$

The advance in time described by the multiplication by e^{tL} requires just the substitution $\hat{x} \to \hat{\phi}$. If one commutes the nonlinear function evaluation and the conditioanl averaging, i.e., writes $\mathbb{P}f(\hat{\phi}) = f(\mathbb{P}\hat{\phi})$ (this is a "mean-field approximation"), and writes furthemore

$$\Phi(t) = \mathbb{P}\hat{\phi} = E[\hat{\phi}|\hat{x}]$$

one finds

$$\mathbb{P}e^{tL}\mathbb{P}Lx_1 = \Phi_2, \quad \mathbb{P}e^{tL}\mathbb{P}Lx_2 = -\Phi_1\left(1 + \frac{1}{1+\Phi_2^2}\right).$$

One can calculate $\mathbb{P}e^{tL}L\mathbb{Q}Lx_j$ for $j = 1, 2$ and find

$$\frac{d}{dt}\Phi_1 = \Phi_2,$$
$$\frac{d}{dt}\Phi_2 = -\Phi_1\left(1 + \frac{1}{1+\Phi_1^2}\right) - 2t\frac{\Phi_1^2\Phi_2}{(1+\Phi_1^2)^2}.$$

The last term represents the damping due to the loss of predictive power of partial data; the coefficient of the last term increases in time and one may worry that this last term eventually overpowers the equations and leads to some odd behavior. This is not the case. Indeed, one can prove the following: If the system (6.16) one starts from is Hamiltonian with Hamiltonian H, and if the initial data are sampled from an initial canonical density conditioned by partial data $\hat{x}$, and if $\hat{H}$ is the renormalized Hamiltonian (in the sense of Chapter 5), then $(d/dt)\hat{H} \leq 0$, showing that the components of $\hat{\phi}$ decay as they should.

The proof requires a minor technical assumption (that the Hamiltonian H can be written as the sum of a function of p and a function of q, a condition commonly satisfied) and we omit it.

There are other ever more sophisticated ways of improving predictions when memory is short. However, in most real-life problems without a marked separation of scales memory is long, indeed often very long. It has been known for a long time that the covariance functions in many important problems decay very slowly; the covariance functions encountered in the Mori-Zwanzig algorithm converge to the covariance functions of the full problem with data drawn from the canonical density as the number of resolved variables decreases and they are also typically long-range in time. The challenge is to devise ways to approximate the Mori-Zwanzig equations under these very common circumstances.

One approach is as follows: As the time t increases, the covariance functions in the equations converge to the covariance functions for the problem without data (that is, $m = 0$, $\hat{x}$ empty). These latter covariance functions, for a given set of equations, can be determined once and for all by Monte-Carlo computation. If one has to solve a fixed set of equations over and over with different data, the computational overhead in the evaluation of these covariances can be justified, and then these covariance functions can be used to approximate the equations in many particular cases. The analysis of such algorithms is beyond the scope of these notes.

6.7. References

1. B. Alder and T. Wainwright, *Decay of the velocity correlation function*, Phys. Rev. A 1, (1970), pp. 1–12.
2. R. Balescu, *Statistical Dynamics, Matter out of Equilibrium*, Imperial College Press, London, (1997).
3. S. Chandrasekhar, loc. cit.
4. A.J. Chorin, O.H. Hald and R. Kupferman, *Optimal prediction and the Mori-Zwanzig representation of irreversible processes*, Proc. Nat. Acad. Sci. USA 97, (2000), pp. 2968–2973.
5. A.J. Chorin, O.H. Hald and R. Kupferman, *Optimal prediction with memory*, Physica D 166, (2002), pp. 239-257.
6. A.J. Chorin and P. Stinis, *Problem reduction, renormalization, and memory*, Comm. Appl. Math. Comp. Sc. 1, (2005), pp. 1-12.

7. D. Evans and G. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic, NY, (1990).
8. G. Ford, M. Kac and P. Mazur, *Statistical mechanics of assemblies of coupled oscillators*, J. Math. Phys. 6 (1965), pp. 504-515.
9. S. Goldstein, *On diffusion by discontinuous movements and on the telegraph equation*, Quart. J. Mech. Appl. Math. 4 (1951), pp. 129-156.
10. G. Givon, R. Kupferman and A. Stuart, *Extracting macroscopic dynamics, model problems and algorithms*, Nonlinearity 17 (2004), pp. R55-R127.
11. S.S. Ma, *Modern Theory of Critical Phenomena*, Benjamin, Boston, (1976).
12. M. Kac, *A stochastic model related to the telegrapher's equation*, Rocky Mountains J. of Math. 4, (1974), pp. 497-509.
13. A. Majda, I. Timofeyev, and E. Vanden-Eijnden, *A Mathematical framework for stochastic climate models*, Comm. Pure Appl. Math. 54, (2001), pp. 891-947.
14. G. Papanicolaou, *Introduction to the asymptotic analysis of stochastic equations, in Modern Modeling of Continuum Phenomena*, R. DiPrima (Ed.), Am. Math. Soc., Providence RI, (1974).
15. P. Stinis, *Stochastic optimal prediction for the Kuramoto-Sivashinksi equation*, Multiscale Modeling Simulation 2 (2004), pp. 580-612.
16. R. Zwanzig, *Problems in nonlinear transport theory*, in L. Garrido (Ed), Systems Far from Equilibrium, Springer, NY, (1980).
17. R. Zwanzig, *Nonlinear generalized Langevin equations*, J. Stat. Phys. 9, (1973), pp. 423-450.